CHARACTERIZATION OF HEAVY, BIODEGRADED CRUDE OILS BY HIGH RESOLUTION ESI FT-ICR MASS SPECTROMETRY

Ryan P. Rodgers[2], Geoffrey C. Klein[1], Lateefah A. Stanford[1], Sunghwan Kim[2] and Alan G. Marshall[1,2]

[1.] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306.
[2.] Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, 1800 E Paul Dirac Drive, Tallahassee, Florida 32310.

Introduction

ESI FT-ICR MS analysis crude oil achieves sufficient mass resolving power ($m/\Delta m_{50\%} > 300,000$, in which $\Delta m_{50\%}$ denotes mass spectral peak full width at half height) and high mass accuracy (< 1 ppm) to allow for the baseline resolution and elemental composition assignment of thousands of heteroatomic species in a single crude oil.[1] The selectivity of the ElectroSpray Ionization (ESI) process limits the observed species to those that both contain one or more heteroatoms (N,S or O) and are acidic (negative ion mode) or basic (positive ion mode). The limitation imposed by ESI is beneficial in that the bulk hydrocarbon matrix is transparent to the analysis, and therefore chromatographic pretreatment for the isolation of polar heteroaromatic species is superfluous. Here we apply ESI FT-ICR MS to a series of heavy crude oils of similar geographic origin that have gone through varying degrees of biodegradation.

Experimental

Crude Oil Samples. Each of six biodegraded crude oils (~20 mg) was dissolved in 10 mL of toluene and then diluted with 10 mL of methanol to a final volume of 20 mL. The samples were further diluted to a final concentration of 0.1 mg of crude/mL of solvent. One mL of the final solution was spiked with 30 μL of ammonium hydroxide to facilitate deprotonation for the ESI FT-ICR mass spectral analysis.

Mass Analysis. The crude oils were analyzed at the National High Magnetic Field Laboratory (NHMFL) with a homebuilt 9.4 Tesla Fourier transform mass spectrometer. Ions were generated externally by a micro-electrospray source and samples were delivered by a syringe pump at a rate of 300 nL/min. Approximately 2.2 kV was applied between the capillary needle and ion entrance (heated metal capillary). The externally generated ions were accumulated in a short (15 cm) rf-only octopole for 30s and then transferred via a 200 cm rf-only octopole ion guide to a Penning trap. Ions were excited by frequency-sweep (100-725 kHz @ 150 Hz/μs at an amplitude of 200 Vp-p across a 10-cm diameter open cylindrical cell). The time-domain ICR signal was sampled at 1.28 Msample/s for 3.27 s to yield 4 Mword time-domain data. One hundred data sets were co-added, zero-filled once, Hanning apodized, and fast Fourier transformed with magnitude computation. Mass spectra were internally calibrated with respect to the most abundant heteroatom containing series over the full mass range. Homologous series were separated and grouped by nominal Kendrick mass and Kendrick mass defect to facilitate rapid identification, as described elsewhere.[2]

Results and Discussion

Variations in the molecular weight distributions are readily observable in the broadband mass spectra shown in Figure 1. As the level of degradation increases (Figure 1, top to bottom) the molecular weight distribution narrows and the average mass shifts to lower m/z.
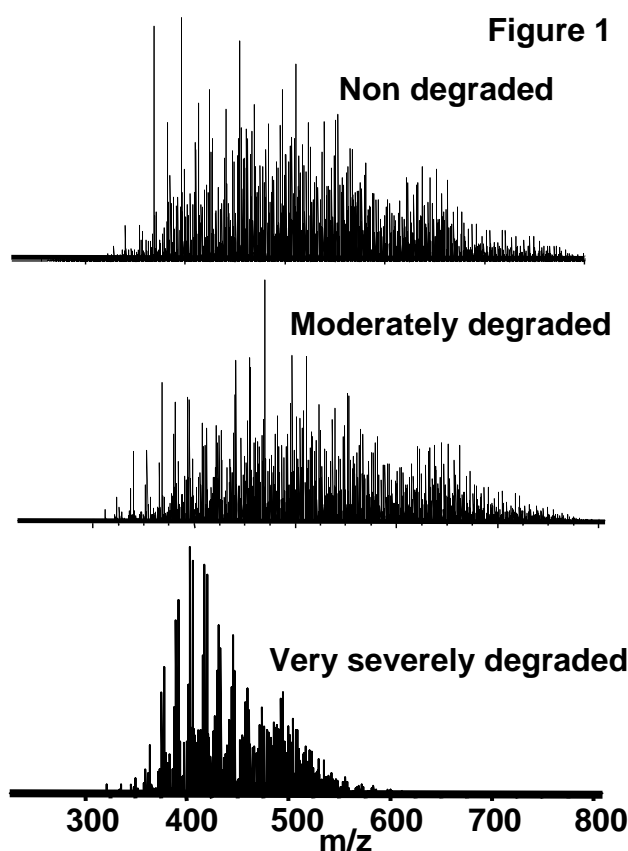

Figure 1

Non degraded

Moderately degraded

Very severely degraded

300   400   500   600   700   800
m/z

Figure 1. Series of broadband negative ion ESI mass spectra for three (undegraded (top), moderately degraded (middle) and very severely degraded (bottom)) members of a series of biodegraded oil samples.

Such changes in the molecular weight distribution provide little information and are easily obtainable from lower resolution mass spectrometers. FT-ICR MS is unique in that the high resolution coupled with the extremely high mass accuracy (less than 1 ppm) allow for the resolution of very closely spaced isobaric doublets (less than 3 mDa) and elemental composition assignment for observed species. Mass resolution is paramount because each mass spectrum is composed of as many as ~8,000 peaks with as many as 20 peaks at a single nominal mass at an average mass resolving power that exceeds 300,000. The assignment of elemental compositions for the thousands of polar heteroaromatic species observed allows for component-by-component monitoring of the compositional changes in the biodegradation samples.

To highlight the compositional changes, three-dimensional van Krevelen diagrams are constructed from the assigned elemental compositions. The van Krevelen diagram facilitates information retrieval from assigned formulas. The plots, constructed from the assigned elemental compositions of peaks corresponding to oxygen containing compounds in the mass spectra, are displayed in Figures 2 and 3. It is clear that there has been substantial change in molecular compositions as the biodegradation of oil proceeds. For the diagram constructed from the spectrum of the non-degraded sample (Figure 2), O_2 species with double bond equivalence (DBE) value of 1 (which are presumably acyclic fatty acids) dominate in abundance. O_2 species with 6 DBE (likely hopanoic acids) are also abundant. The sample is also rich in highly cyclic or aromatic fatty acid type molecules. The diagram (Figure 3) from the severely degraded oil, shows a shift in dominance of O_2 type abundance from a DBE value

of 1 to a DBE value of 2-4 (presumably mono-, di- and tri- cyclic naphthenic acid). From this pattern of change, we propose that ratio of acyclic to cyclic naphthenic acid can be used as an indicator of biodegradation.
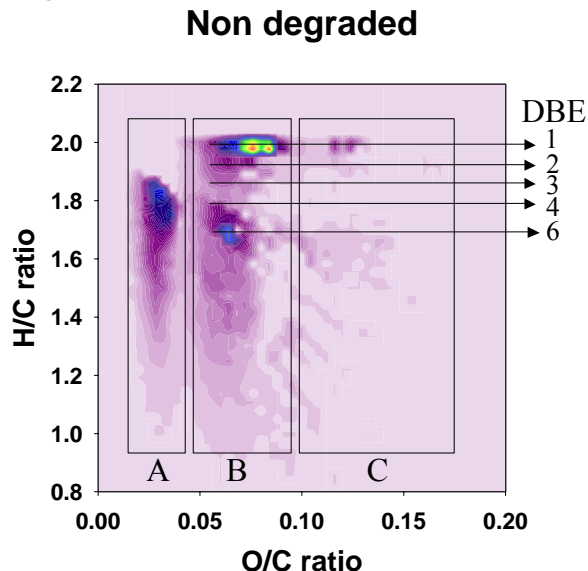
Non degraded

Figure 2. Van Krevelen diagram of O containing compounds in non degraded oil sample. A, B, C each represent O, O_2 and O_3 or more oxygenated species.
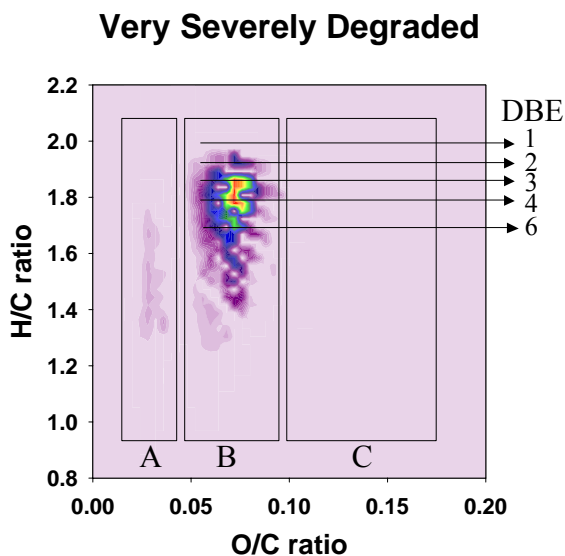
Very Severely Degraded

Figure 3. Van Krevelen diagram of O-containing compounds in a very severely degraded oil sample. A, B, C represent O, O_2 and O_3 or more oxygenated species.

The van Krevelen diagrams, constructed from the assigned elemental compositions of peaks corresponding to nitrogen containing compounds in the mass spectra, are displayed in Figures 4 and 5. For nitrogen containing compounds, there is a slight shift in the most abundant species to those with lower H/C ratios as biodegradation proceeds, suggesting that N-containing compounds with more condensed ring type structures are more resistant to biodegradation. A more complete picture, including all classes, types and carbon number distributions will be presented.
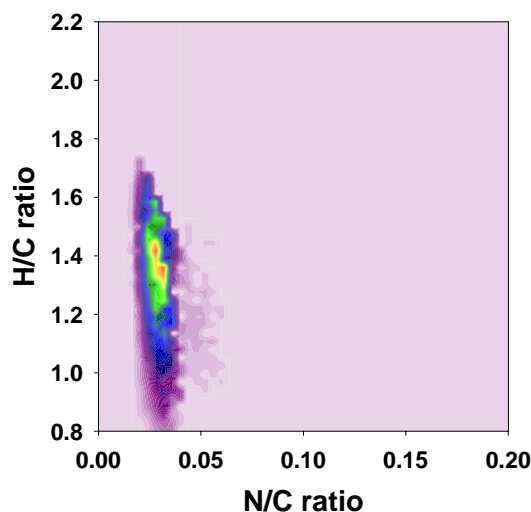
Non degraded

Figure 4. Van Krevelen diagram of N-containing compounds in a non-degraded oil sample.
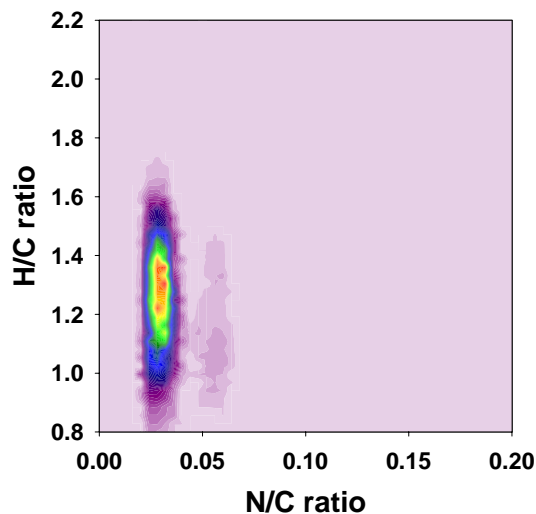
Very severely degraded

Figure 5. Van Krevelen diagram of N-containing compounds in a very severely degraded oil sample.

References
1. Qian, K; Robbins, W. K.; Hughey, C. A.; Cooper, H. J.; Rodgers, R. P.; Marshall, A. G., *Energy and Fuels,* **2001**, 1505-1511
2. Hsu, C. S.; Qian, K.; Chen, Y. C., *Analytica Chimica Acta,* **1992**, 79-89.